

CLAIMS

1. Additives for hydrogenated resins, formed by functionalized perfluoropolyethers and functionalized polyolefins, said additives obtainable by using the following components:
 - a) bifunctional perfluoropolyethers having a -COOR end group optionally in admixture with monofunctional perfluoropolyethers having -COOR end group, wherein $R = H, C_1-C_{10}$ alkyl, the number average molecular weight of bifunctional and monofunctional perfluoropolyethers being in the range 500-5,000, preferably 900-3,000;
 - b) mono, bi or polyfunctional hydrogenated monomers having functional groups capable to react with the -COOR end groups of the compound a); preferably said functional groups of the hydrogenated monomers are aminic groups,
 - c) polyolefins having functional groups, preferably formed by C_2-C_4 monomers, wherein said functional groups are capable to react with the block oligomer/polymer obtained by reaction of a) with b), preferably said functional groups being obtained by grafting with maleic anhydride;reacting in a first step a) with b), or a) with mixtures

of monomers b) having a different functionality, until disappearance of the -COOR group of component a), and in a second step the product obtained from the reaction of a) with b) with the functionalized polyolefins c).

2. Additives according to claim 1, comprising neutral perfluoropolyether oils having a molecular weight in the range 2,000-10,000 (compound d)).

3. Additives according to claims 1-2, wherein the amounts of each component a)-d), expressed as percentages by weight, are the following:

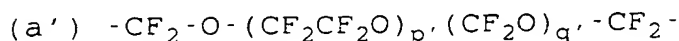
- component a) 30-70% by weight;
- component b) 1-30% by weight;
- component c) 10-70% by weight;
- component d) 0-20% by weight;

the sum of a) + b) + c) + d) being equal to 100% by weight.

4. Additives according to claims 1-3, wherein the bifunctional (per)fluoropolyethers and the monofunctional perfluoropolyethers mentioned in a) have one or more of the following units statistically distributed along the chain:
 (C_3F_5O) ; $(CF_2(CF_2)_{x'}CF_2O)$ wherein x' is an integer equal to 1 or 2; $(CFYO)$ wherein Y is F or CF_3 ; (C_2F_4O) ; $(CR_4R_5CF_2CF_2O)$ wherein R_4 and R_5 are equal to or different from each other and selected between H, Cl, and wherein

one fluorine atom of the perfluoromethylene unit is optionally substituted with H, Cl or (per)fluoroalkyl having from 1 to 4 carbon atoms.

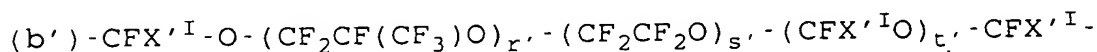
5. Additives according to claim 4, wherein the preferred bifunctional compounds of a) are the following, with the perfluorooxyalkylene units statistically distributed along the chain:



(VIII)

wherein:

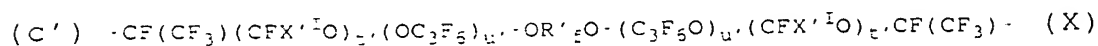
p' and q' are numbers such that the q'/p' ratio is comprised between 0.2 and 2 and the molecular weight is in the above mentioned range;



(IX)

wherein:

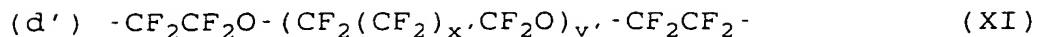
X'^I is $-F$ or $-CF_3$; r' , s' and t' are numbers such that $r' + s'$ is in the range 1-50, the $t'/(r' + s')$ ratio is in the range 0.01-0.05, $r' + s'$ being different from zero, and the molecular weight is in the above mentioned range;



wherein:

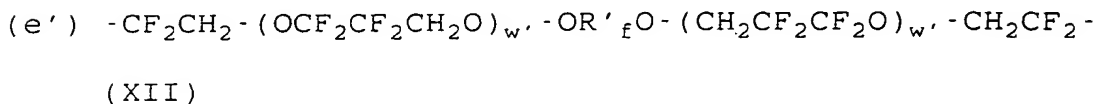
R'_f is a C_1 - C_3 perfluoroalkylene; $u' + t'$ is a number

such that the molecular weight is in the above range; t' can also be equal to zero; X'^I is as above indicated;



wherein:

v' is a number such that the molecular weight is in the above range, x' is an integer equal to 1 or 2;

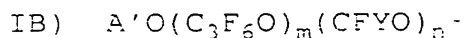


wherein:

R'_f is a C_1 - C_8 perfluoroalkylene; w' is a number such that the molecular weight is in the above range;

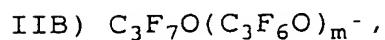
the end groups of the bifunctional perfluoropolyethers component a) being of the $-COOR$ type wherein $R = H$ or C_1 - C_{10} alkyl.

6. Additives according to claim 4, wherein the monofunctional perfluoropolyethers used in a) in admixture with bifunctional perfluoropolyethers have the following structures:

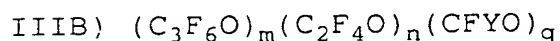


wherein Y is $-F$, $-CF_3$; $A' = -CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, C_2F_4Cl ; the C_3F_6O and $CFYO$ units are randomly distributed along the (per)fluoropolyether

chain, m and n are integers, the m/n ratio is ≥ 2 , m and n have values such that the molecular weight is within the limits indicated for component a);



wherein m is a positive integer and is such that the number average molecular weight is in the limits indicated for component a);



wherein:

Y is equal to -F, -CF₃; m, n and q, different from zero, are integers such that the number average molecular weight is in the limits indicated for component a);

being the end group of the monofunctional perfluoropolyethers -CF₂-COOR, R being as above.

7. Additives according to claims 1-6, wherein the amount of monofunctional perfluoropolyethers in the mixture with the bifunctional perfluoropolyethers in a) is in the range 0-90% by weight.
8. Additives according to claims 1-7, wherein the monomers component b), when the functionality is aminic, are the following:

(b1) monoamines of formula R₁-NH₂ wherein R₁ is a linear aliphatic or cycloaliphatic C₁-C₂₀ alkyl with a num-

ber of carbon atoms of the ring from 4 to 6, optionally substituted with C_1 - C_4 alkyl groups; or R_1 is an aryl group optionally substituted with linear or branched C_1 - C_4 alkyl groups, the total number of the carbon atoms being in the range 6-20;

(b2) diamines of formula $NR_{2A}R_{3A}-R_{1A}-NH_2$, wherein R_{1A} = linear or cycloaliphatic C_2 - C_{12} alkyl radical with a number of carbon atoms of the ring from 4 to 6, optionally substituted with C_1 - C_4 alkyl groups, or C_6 - C_{12} aryl group; R_{2A} and R_{3A} , equal to or different from each other, are hydrogen or linear or branched C_1 - C_5 alkyl group;

(b3) aromatic tetramines of formula $(NH_2)_2-Ar1-Ar1-(NH_2)_2$ with $Ar1$ = phenyl, optionally substituted with C_1 - C_4 alkyl groups.

9. Additives according to claim 8, wherein the component b) is selected from stearylamine (b1), a compound selected from the classes (b2) and (b3).
10. Additives according to claims 1-9, wherein in component c) the functionalized polyolefins are selected from the following polymers:
polypropylene homopolymer, copolymers of polypropylene, high density polyethylene (HDPE), linear low density polyethylene (LLDPE) grafted with functionalized monomers

capable to react with the aminic groups of the reaction product of a) + b), preferably the grafting monomer is the maleic anhydride; or

copolymers or terpolymers of ethylene containing an ethylene monomer having a second functional group selected from vinyl acetate (VA) butylacrylate (nBA) and carbon oxide (CO).

11. Additives according to claims 1-10, wherein the perfluoropolyether oils component d) have the units in the chain according to claims 4-6 and the end groups are perhalogenated of the $-\text{CF}_2\text{X}$ type, with $\text{X} = \text{F}, \text{Cl}$, preferably $\text{X} = \text{F}$.
12. A process for obtaining the additives according to claims 1-11, comprising the following steps:
 - 1) synthesis of the compound a) + b) by reaction of the functionalized perfluoropolyether component a), optionally formed by a mixture of a bifunctional and monofunctional perfluoropolyether, with the hydrogenated monomer component b), by heating under stirring at a temperature in the range $90^\circ\text{-}100^\circ\text{C}$, and subsequently at $100^\circ\text{-}130^\circ\text{C}$ under vacuum (1 mmHg) to complete the reaction, i.e. until in the IR spectrum the band at 1800 cm^{-1} of the COOR group linked to $-\text{CF}_2-$ disappears;

- 2) addition, under stirring, in the same reactor, of the functionalized polyolefin component c), preferably functionalized with maleic anhydride, and reaction of the mixture by heating at atmospheric pressure for 30-60 minutes at a temperature in the range 180°C-190°C.
13. A process according to claim 12, wherein the molar ratio between the functional groups of b) and of a) is in the range 1-1.5, and the amount of b) is such to give rise in the reaction to the disappearance of the -COOR groups of a).
14. A process according to claims 12-13, wherein to the compound obtained in the first step fluorinated additives component d) are added.
15. A process according to claims 12-14, wherein in the second step the ratio between the functional groups of the compound obtained by reaction of a) with b) and the functional groups of the functionalized polyolefin ranges from 10 to 0.1 by moles.
16. Use of the additives according to claims 1-11, as additives for hydrogenated resins.
17. Masterbatches comprising the additives of claims 1-11, and hydrogenated resins.
18. Masterbatches according to claim 17, wherein the additive

concentration is in the range 1-50% by weight.

19. Manufactured articles obtainable by mixing the masterbatches according to claims 17-18 with hydrogenated resins.